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H. A. Laitinen, University of Illinois

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SUMMARY

1. Hydrazine and water are polarographically inert in liquid ammonia solution at mercury and platinum electrodes.

2. A neutral solution of chloramine in liquid ammonia may be prepared by the passage of chlorine into a suspension of sodium amide. Many other preparative methods lead to contamination by ammonium salts.
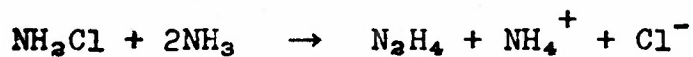
3. Chloramine yields a well-defined reduction wave at dropping mercury and rotating platinum electrodes. Observation of the diffusion current is a convenient means of following changes in the concentration of chloramine in liquid ammonia solutions.

4. Unlike the alkali metal cations whose behavior it parallels at a mercury electrode, the ammonium ion is reducible at a platinum electrode in liquid ammonia at -78°C.

5. The use of a rotating platinum electrode in liquid ammonia is described. The electron electrode was used as reference.

6. Under polarographic conditions, solutions of chloramine in liquid ammonia are unstable at -36°C., decomposing with a half-life of the order of one or two hours. At -78°C., such solutions are stable for days. Hydrazine accelerates the decomposition.

7. The kinetics of chloramine decomposition in liquid ammonia are partially explicable in terms of the following autocatalytic mechanism:

$$NH_2Cl + 2NH_3 \longrightarrow N_2H_4 + NH_4^{+} + Cl^{-}$$
$$NH_2Cl + N_2H_4 \longrightarrow N_2H_2 + NH_4^{+} + Cl^{-}$$
$$NH_2Cl + N_2H_2 \longrightarrow N_2 + NH_4^{+} + Cl^{-}$$
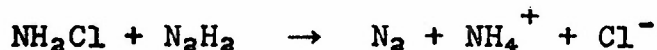
8. The electroreduction process of chloramine is a two-electron process. The interference between this electrode process and that of ammonium ion reduction gave rise to earlier reports of a single electron reduction.

Review of Early Work

The initial investigations were concerned with a polarographic study of solutions containing metal cations in anhydrous liquid ammonia at $-35\,^{\circ}C$. The dropping mercury electrode was used to determine the current-voltage behavior of the divalent ions of cobalt, nickel, zinc and cadmium and the trivalent cations of aluminum, chromium and cobalt.

The results and conclusions of these investigations have been described in the literature.[1]

Recent Investigations

The more recent studies have been primarily directed towards a study of the chemical and electrochemical properties of solutions of chloramine in liquid ammonia. Towards this end, a technique has been developed for the use of a rotating platinum microelectrode in this solvent; the dropping mercury electrode has also been employed.

Secondary studies have included an investigation of suitable methods of chloramine preparation. The electrochemical behavior of dilute solutions of hydrazine and of water in liquid ammonia have also received attention.

Polarographic Behavior of Ammonia Solutions of Hydrazine and Water

Both these compounds were found to be polarographically inert at both dropping mercury and rotating platinum electrodes, under all experimentally permissible conditions. For a mercury electrode, the useful potential range is limited anodically by the dissolution of mercury and cathodically (using tetrabutylammonium salts as supporting electrolytes) by the potential of electron dissolution. A similar cathodic limit is encountered with a platinum electrode but the anodic range is extended considerably to the potential of nitrogen evolution. In strongly acidic solutions (i.e. containing a large ammonium ion concentration), the cathodic limit is the potential of discharge of the ammonium ion. Only mildly basic solutions have been investigated, since the amides of most common cations are only slightly soluble.

Since ammonium ion can be readily detected as a reducible species yielding a cathodic wave on a current-voltage plot,[2] the inactivity of hydrazine and water at a cathode in liquid ammonia and demonstrates that the reactions:

$$H_2O + NH_3 \rightarrow OH^- + NH_4^+ \tag{1}$$

and

$$N_2H_4 + NH_3 \rightarrow N_2H_3^- + NH_4^+ \tag{2}$$
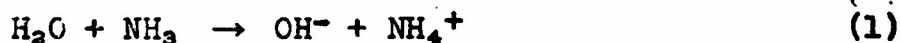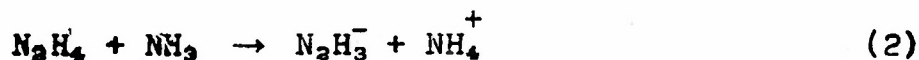
cannot proceed to any appreciable extent. Furthermore, since the addition of hydrazine to mildly acidic ammonia solutions yielded no diminution of the ammonium ion wave height, it can be concluded that the reaction:

$$N_2H_4 + NH_4^+ \rightarrow N_2H_5^+ + NH_3 \tag{3}$$
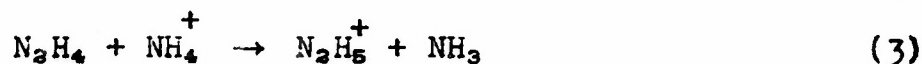
does not occur. This conclusion would be invalidated if the hydra-zonium ion is found to reduce at a potential not far removed from the reduction potential of ammonium ions.

THE PREPARATION OF CHLORAMINE

Chloramine is unstable and no method for the preparation of the pure compound has been devised. The physical properties of chloramine are very inadequately understood.

For the electrochemical studies that are described below it was desired to introduce, into a solution of a supporting electrolyte in liquid ammonia, some substance, or substances, that would yield a moderate concentration of chloramine. A further desirable condition was that this addition should cause no alteration of the acidity of the solution. Alternatively, it would have been adequate if the introduction of chloramine and ammonium ion could have been made in some determinable ratio, provided that the NH_2Cl/NH_4^+ ratio was not to small.

With these criteria in mind, the following methods for the preparation and introduction of chloramine were employed.

Method A

Chloramine was prepared by the reaction of ammonia with sodium hypochlorite in aqueous solution:[12]

$$NH_3 + OCl^- \rightarrow NH_2Cl + OH^- \tag{4}$$
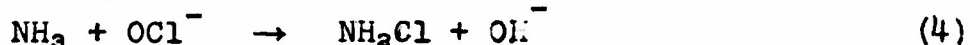
and extracted with ether. After freeze-drying, the extract was added directly to the liquid ammonia solution.

The chief objection to this method is the undesirable presence of ether in the electrolytic cell. Moreover, there is a possibility that appreciable quantities of water and inorganic salts are concurrently introduced.
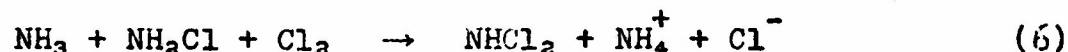
Method B

Chloramine was prepared by the direct introduction of chlorine, from a hypodermic syringe, into the polarographic cell
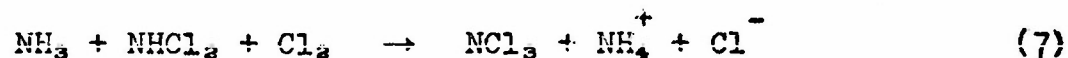
$$Cl_2 + 2NH_3 \rightarrow NH_2Cl + NH_4^+ + Cl^- \tag{5}$$
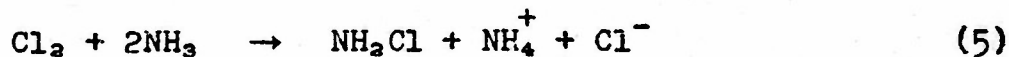
In spite of the violence of reaction (5),[13] or possibly because the local heating produced by it was sufficient to vaporize ammonia in the neighborhood of the reaction zone, it proved difficult to prevent bubbles rising to the surface, carrying ammonium chloride "fog" (and possibly also gaseous chloramine) with them. The highest yield of chloramine produced by this method was 40% calculated with the assumption that chloramine is reducible by a two electron mechanism.

In this method of preparation, local excess of chlorine may give polychloramines;

$$NH_3 + NH_2Cl + Cl_2 \rightarrow NHCl_2 + NH_4^+ + Cl^- \tag{6}$$

and

$$NH_3 + NHCl_2 + Cl_2 \rightarrow NCl_3 + NH_4^+ + Cl^- \tag{7}$$

These di- and trichloramines are most probably ammonolysed to monochloramine, but should this reaction be slow, this method constitutes an explosion hazard if nitrogen trichloride is formed in appreciable amounts. The method was abandoned for this reason and because it was

found that an unpredictable excess of ammonium ion was produced, in addition to the stoichiometric quantity predicted by (5).

Method C

The side reactions (6) and (7) of the interaction of chlorine with liquid ammonia were obviated by diluting the chlorine with a large excess of nitrogen. In these experiments, chlorine was bled into a nitrogen stream from a gas buret, using dibutyl phthalate as the manometric liquid. Though chlorine is appreciably soluble in this ester, the rate of solution is slow.

This method was quite successful since a large percentage of the ammonium chloride was carried away by the nitrogen stream as suspended solid. The uptake into the ammonia frequently occurred with a NH_2Cl/NH_4^+ ratio of greater than unity; however the exact ratio depended largely on bubble size and flow rate and so was not reproducible.

Method D

An apparatus was devised for the steady preparation of a chloramine-containing gas stream by direct reaction of chlorine and ammonia in the gas phase.

A stream of chlorine was mixed with a three-fold excess of nitrogen and passed through a glass-wool plug to assure homogeneity. This mixed stream was then led into a mixing chamber into which ammonia was also flowing, such that the volume ratios $Cl_2:N_2:NH_3$ were approximately 1:3:12. This large dilution was necessary to prevent the formation of polychloramines and to prevent the temperature of the reaction zone reaching a height at which chloramine might be
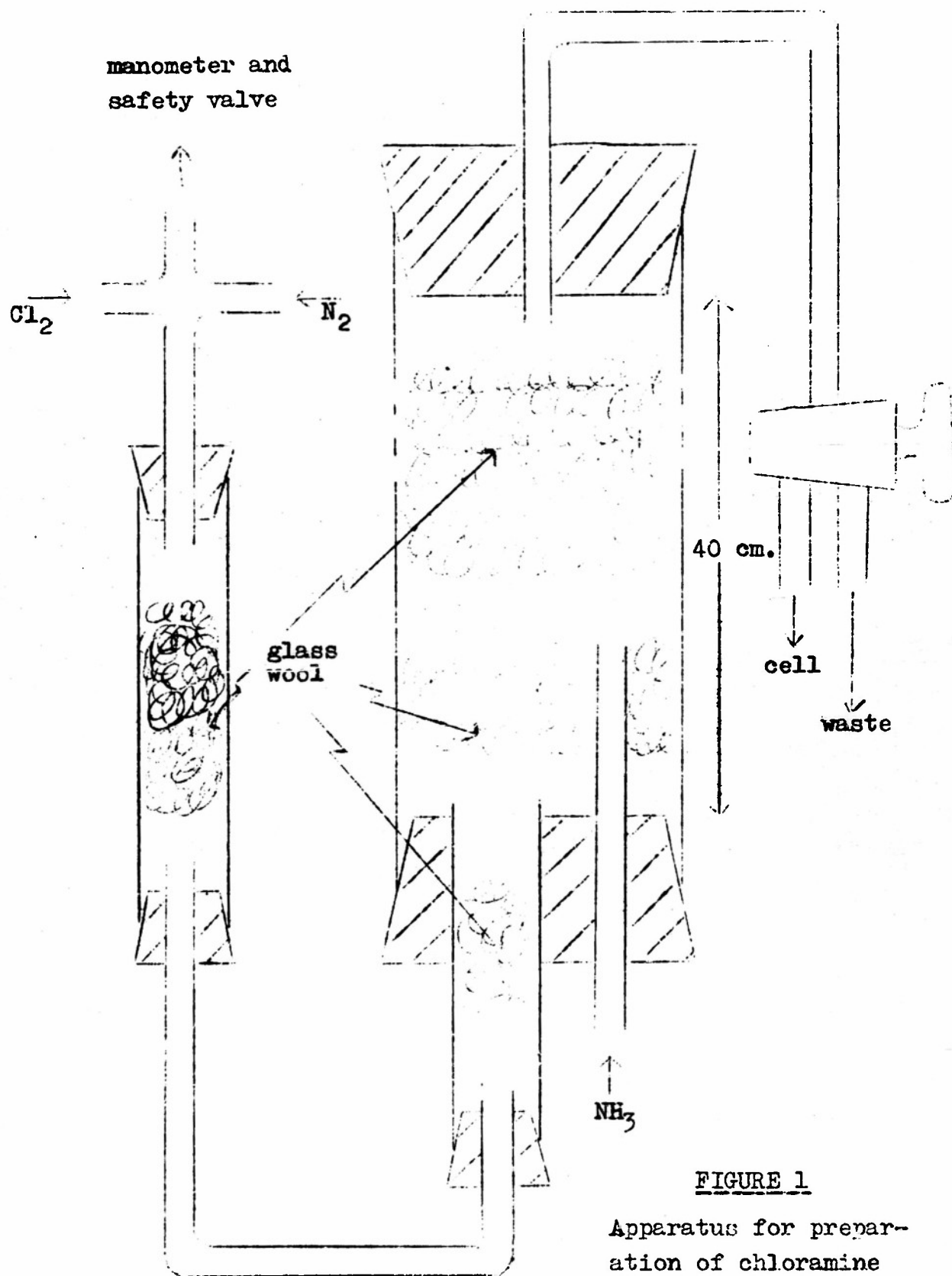
manometer and
safety valve

Cl_2 N_2

glass
wool

40 cm.

cell

waste

NH_3

FIGURE 1

Apparatus for prepar-
ation of chloramine
by method D

supposed to undergo rapid decomposition. The design of the mixing chamber is important, since it was found that the solid ammonium chloride that is a reaction product could easily form an impervious plug across a 1 cm. diameter inlet tube. The reaction, (5), yields ammonium chloride particles in extremely fine dispersion, such that a glass-wool-packed tube, 20 cms. in length, is required as an adequate filter. The apparatus is shown in Figure 1. A sample of the issuing gases, after the system had reached a steady state, was passed into the cell.

Although this method is a very convenient means for producing chloramine, the product was found to be contaminated by about 10% of ammonium chloride. This impurity may have resulted from inefficient filtration; however it is thought more likely to have been produced by gas phase decomposition of the chloramine-ammonia mixture. Other investigators[11] have shown that hydrazine is not a product of this reaction.

Method E

It has been reported[14,15] that considerable yields of chloramine (and, eventually, of hydrazine) are produced by the reaction with liquid ammonia of ether solutions of tertiary-butyl hypochlorite. The primary reaction is presumably:

$$NH_3 + (CH_3)_3COCl \rightarrow NH_2Cl + (CH_3)_3COH \tag{8}$$
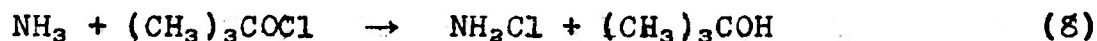
Hence it was hoped that addition of the pure hypochlorite to a liquid ammonia solution would yield a neutral solution of chloramine. This was found to be the case. Unfortunately, however, under

the experimental conditions employed and at $-78°C.$, reaction (8) was found to be slow as indicated by the increase of chloramine concentration with time, or upon the addition of ammonium acetate which presumably functions as a catalyst.

Method F

Reports of the volatility of chloramine from liquid ammonia suggested another method of introduction. An ammonia solution of chloramine was prepared by Method C. A portion of this solution was then distilled into the cell.

It was found that chloramine was quite volatile but that the resulting solution was contaminated with ammonium ions. Either a physical carry-over of ammonium chloride had occurred or some of the chloramine had decomposed while in the gas phase, as suggested in Method D. A similar result was observed when nitrogen was passed through the chloramine-containing ammonia solution at its boiling point.

Method G

The possibility that the ammonium chloride contamination observed in Method F was due to carry-over, suggested that this difficulty could be overcome by distillation from neutral solutions of chloramine.

Sodium amide is very sparingly soluble in liquid ammonia[16] $(10^{-3}$ moles/liter at $25°C.)$ and hence a solution in contact with solid sodium amide will remain essentially neutral upon introduction of a modest amount of chlorine. Hence a chlorine-nitrogen mixture was passed into an ammonia solution standing over excess sodium

amide and a portion of the solution was distilled into the polaro-
graphic cell. However, there was no evidence for appreciable concen-
tration of either chloramine or ammonium ions in the distillate.

The distillation was repeated using sodium amide prepared by
the prolonged reaction of sodium metal with liquid ammonia, to
eliminate the possibility that the chloramine was decomposed by
impurities present in commercial sodium amide. There was no improve-
ment in results by this means, or by attempting to entrain the
chloramine in a nitrogen stream.

Other experiments (see Method H) showed that chloramine is
stable in these very slightly basic ammonia solutions. Hence it must
be supposed that there is a decrease in chloramine vapor pressure on
reducing the acidity of a chloramine solution, possibly because of
the formation of the chloramide ion, $NHCl^-$.

Method H

A solution of chloramine in neutral ammonia was prepared by
the passage of a chlorine-nitrogen stream into a suspension of sodium
amide in a saturated solution of sodium acetate in liquid ammonia at
$-78°$ C. The vessel employed was equipped with a filter-tube siphon
by which a portion of the supernatant liquid could be drawn off and
added directly to the electrolytic cell.

Although the introduction of a liquid ammonia solution to the
cell presents greater experimental difficulties than the passage of a
gaseous reagent, this method proved to be an excellent means of intro-
duction of neutral chloramine. No evidence for an increase in the
acidity of the cell solution was obtained, provided that no

appreciable vaporization of the reagent occurred during its addition.

POLAROGRAPHY OF CHLORAMINE IN LIQUID AMMONIA

Two types of electrode system were employed in this investigation: the dropping mercury electrode, with mercury pool reference and the rotating platinum microelectrode, with electron electrode reference. The experiments with the latter system were mainly exploratory, having a view to determining the suitability of the system for polarographic investigations in liquid ammonia. The experimental details and the results obtained will be reported separately for the two types of electrode system.

Dropping Mercury Electrode - Experimental

The polarographic cell employed in these experiments is shown diagrammatically in Figure 2; its capacity was about 50 ml. The lower portion of the cell was immersed in a solid carbon dioxide - ethyl cellosolve bath contained in a 2-gallon Dewar flask.

The cell was subjected to high vacuum for about one hour with the electrode in position, the requisite amount of supporting electrolyte having been previously introduced. Ammonia was then condensed in the cell after distillation from potassium metal in a vacuum system, the initial and final samples being rejected. This treatment serves to remove water and many other impurities possibly present in the tank ammonia. However, experiments indicated that this pretreatment was unnecessary and hence, in some experiments, tank ammonia was condensed directly into the cell.

After a few minutes boiling to ensure homogeneity of the

waste
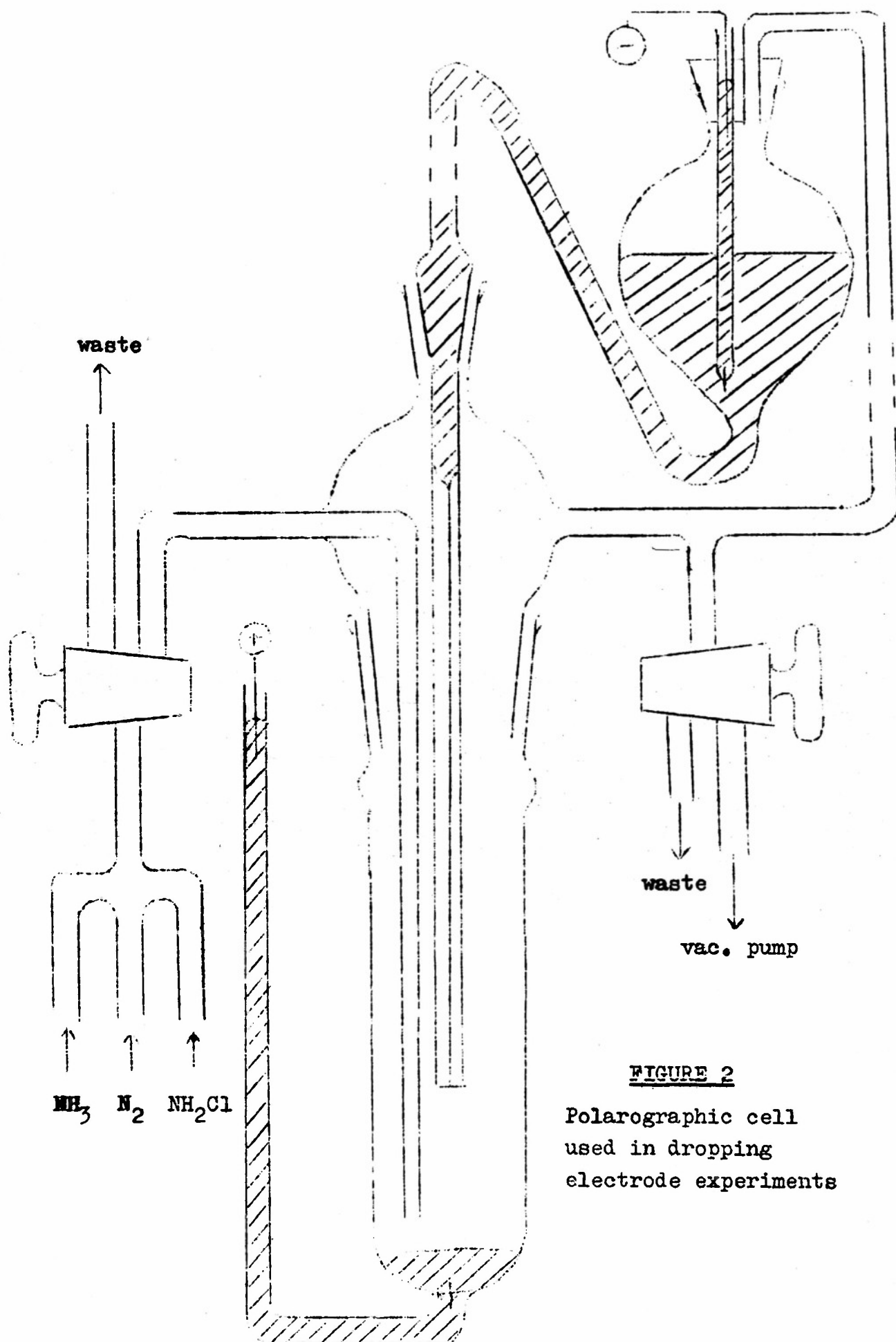
NH_3 N_2 NH_2Cl

waste

vac. pump

FIGURE 2

Polarographic cell
used in dropping
electrode experiments

solution, followed by a few minutes standing to achieve thermal equilibration, a residual polarogram was run, employing a Sargent Model XXI Polarograph. In general, this residual curve exhibited a small wave at about -1.6 volts versus the pool anode,[4] indicating the presence of ammonium ion in varying small concentrations.[2] This ammonium ion was derived either from ammonium salts deposited during previous experiments in inaccessible parts of the apparatus or possibly from acidic impurities in the supporting electrolyte.

All polarograms were performed with the cell thermostated manually at -36 ± 0.5 °C. at which temperature the vapor pressure of ammonia is slightly less than atmospheric and yet no difficulties are encountered in the freezing of mercury.

At this stage the chloramine was introduced. During the series of experiments, the results of which are reported in the following section, Method D was usually employed to prepare chloramine. Immediately after the introduction, the solution was boiled to ensure thorough mixing of the cell contents and to expel dissolved nitrogen. As soon as possible thereafter, the first polarogram was run and subsequent polarograms were recorded during the following 4 to 8 hours.

Potassium chloride, ammonium chloride or tetrabutylammonium iodide was used as supporting electrolyte. The process limiting the cathodic range of the polarogram was, for potassium and ammonium chloride, the reduction of the cation to the corresponding amalgam.[2,] Tetrabutylammonium salts are not reduced and electron dissolution is the terminal process;[3] the use of these supporting electrolytes enabled the ammonium reduction wave to be recorded. Alkali metal cations are reduced at a more positive potential than is ammonium ion

and hence use of alkali metal salts as supporting electrolyte obscures
the ammonium ion reduction wave.

## Dropping Mercury Electrode - Results

Chloramine was observed to give a single reduction wave in
liquid ammonia, with a half wave potential of approximately - 0.5
volts versus the pool anode (+0.15 volts versus the normal hydrogen
electrode). The diffusion current, i_d, was well defined except in the
more concentrated solutions where a maximum was found to obscure the
initial section of the plateau. The value of N required to satisfy
the equation $E_{1/2} - E = \frac{RT}{NF} \ln(i_d - i)/i$ was about 0.3, indicating an
irreversible electrode process.

At -35° C., chloramine was found to be unstable in the polaro-
graphic solutions, as evidenced by the decrease of the chloramine wave
height with time. It must be pointed out that none of the methods of
preparation of chloramine permit an accurate estimation of the chlor-
amine concentration in the cell. However, since the chloramine reduc-
tion wave is diffusion controlled, the concentration of chloramine was
directly proportion to the wave height (after subtraction of the
residual current) and hence relative concentrations could be deter-
mined with accuracy. Moreover, since the same capillary was used
throughout, with approximately the same mercury head, it was possible
to compare concentrations in different experiments to an adequate
precision.

Two types of polarogram were employed. In the first type, a
steadily increasing negative potential was applied across the cell
such that the dropping electrode potential was varied continuously
from +0.1 volt versus the pool (at which potential there is a large

anodic current due to mercury dissolution) to the potential of reduction of the cation of the supporting electrolyte (or, in the case of the tetrabutylammonium supporting solutions, to the potential of electron dissolution). About 15 minutes were required for the recording of such a polarogram and a repetition of this procedure enabled the complete course of decomposition to be followed. The second type of polarogram was recorded while applying a constant potential to the dropping electrode, this potential corresponding to a convenient point on the plateau of the chloramine (or ammonium ion) wave. This type of polarogram (after residual subtraction) represented, in effect, a direct plot of chloramine concentration versus time. In certain cases, both types of polarogram were used to investigate the kinetics of the decomposition; both procedures gave the same result. This last piece of evidence, together with the observed fact that decomposition proceeded at the same rate whether or not the cell was allowed to pass current, indicated that the electrode processes had no bearing on the course of decomposition of chloramine in the bulk of the solution.

Experiments in which potassium chloride was used as supporting electrolyte were limited to observing the change with time of the height of the chloramine wave and this study was also made with the other supporting electrolytes. The diffusion current decreased with time until eventually only a residual current remained. Plots were made of log i_d versus time, with a view to determining whether the decomposition was first-order; these plots are shown in Figure 3. Second-order plots of $1/i_d$ versus time were markedly non-linear. Deviations from linearity for the first-order plots were frequently observed towards the end of experiments, in the sense that the

FIGURE 3

First-order plots for
chloramine decomposition.
Experiment numbers
are circled.
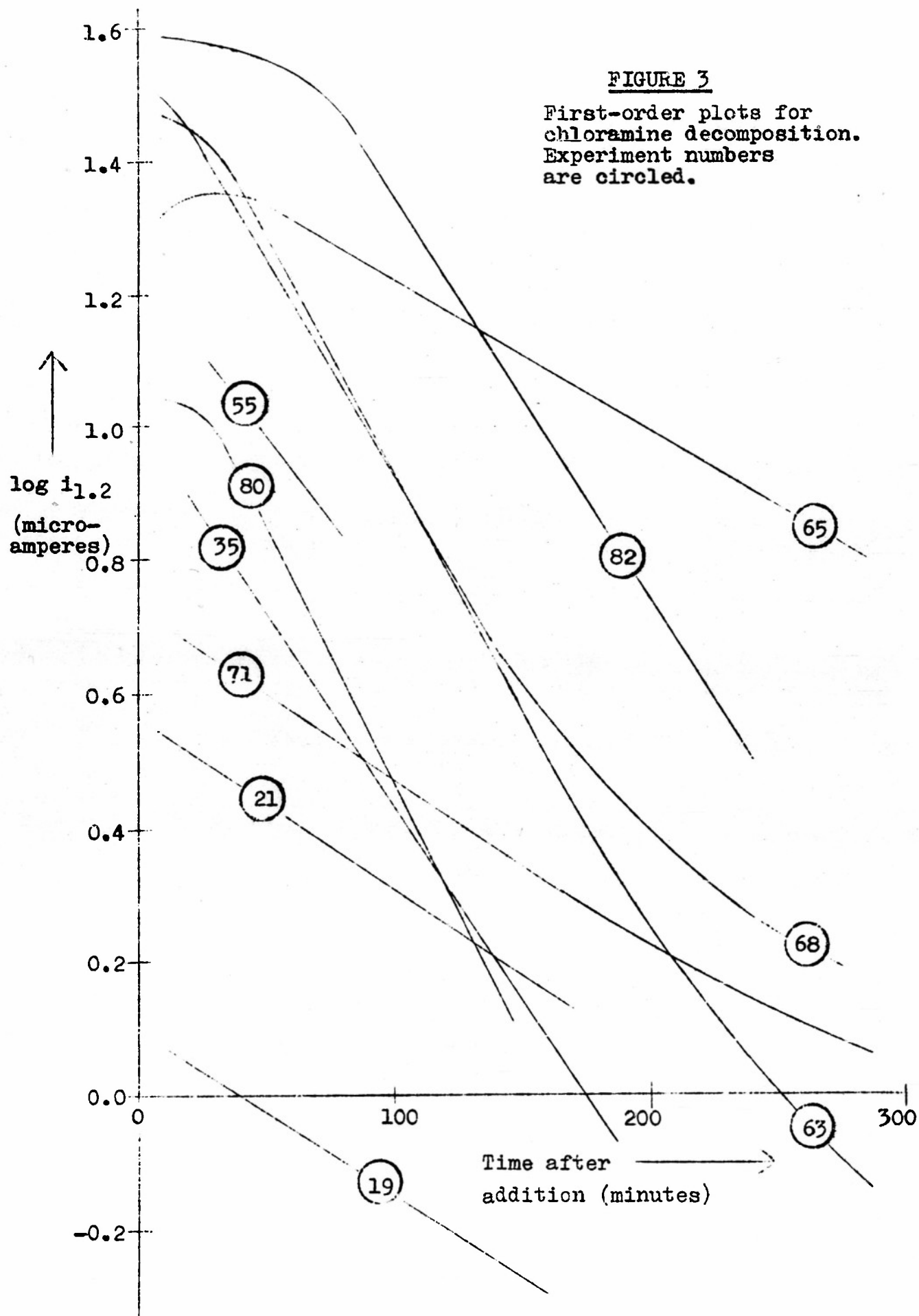
apparent half-life increased with time. Such an effect can be satis-
factorily attributed to under-correction for residual current. In
cases where the chloramine wave was allowed to decay to essentially
zero, it was found that a greater residual current remained than
before the introduction of the chloramine; subtraction of this final
residual current restored the linearity of the log i_d versus t plot.

At the higher concentrations of chloramine, a region of
curvature of the first-order plots is initially observed during which
the rate of decomposition is several times slower than subsequently.
At lower concentrations this period of curvature either does not exist
or has a duration of less than ten minutes. At the end of one hour,
all plots are essentially linear (apart from residual under-correction
in certain cases) and the half-life of decomposition is constant. The
values of this half-life are listed in Table 1. It will be seen that
the half-life values fall into two groups: 49 ± 6 minutes and 127 ± 10
minutes, and that this variation cannot be correlated with the concen-
trations of ammonium ion, chloride ion, iodide ion or the cation of
the supporting electrolyte. Other experiments showed that the half-
life was not markedly altered by changes in water concentration, the
concentration of mercuric ion or in the area of the mercury pool.

Figure 4 shows an example of a chloramine reduction wave in
ammonium chloride solution. It will be observed that a "shoulder"
exists to the ammonium ion reduction curve. This could represent a
reduction wave of a species the half-wave potential of which is some-
what more positive than the ammonium ion decomposition potential.
Similarly, a "prewave" was sometimes found more positive than the
ammonium wave in polarograms of solution containing tetrabutylammonium
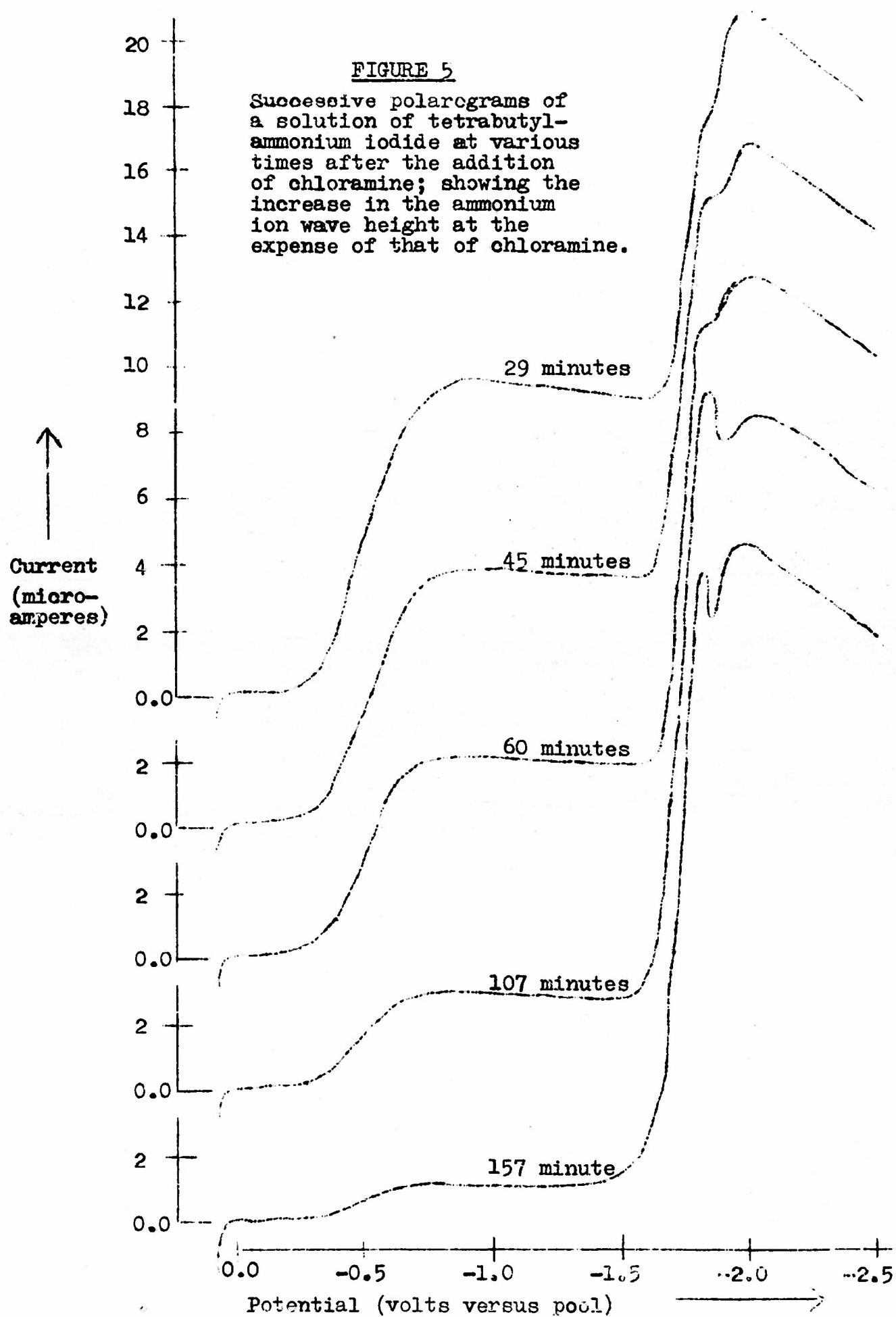
FIGURE 4

Polarogram of Chloramine in
ammonium chloride solution
in liquid ammonia. Lower
curve represents residual
current.
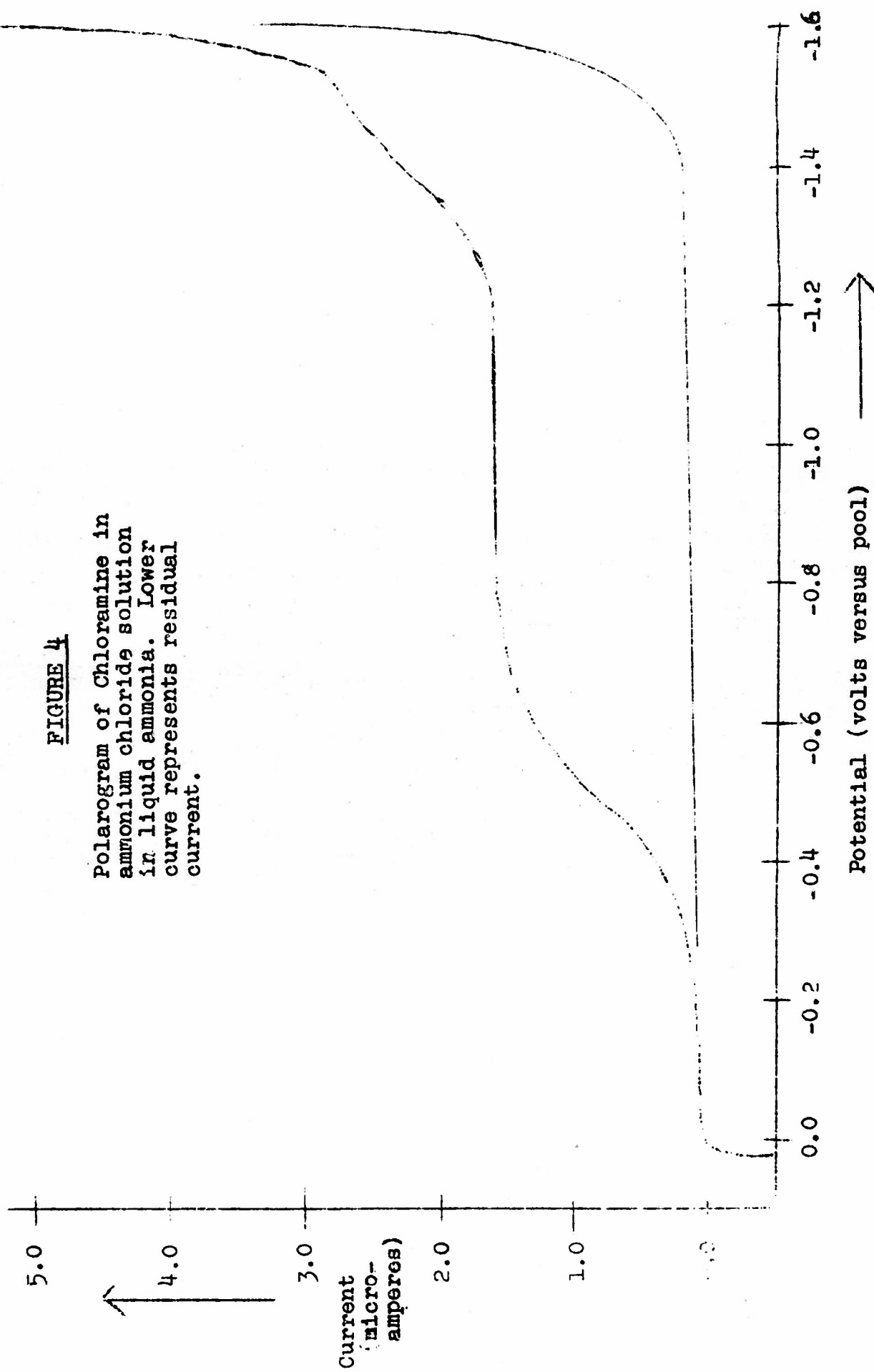
iodide supporting electrolyte. This behavior was irreproducible and no explanation can be proffered.

The use of tetrabutylammonium iodide as supporting electrolyte enabled the ammonium reduction wave height to be studied simultaneously with that of chloramine. Figure 5 shows three typical polarograms recorded at 29, 45 and 60 minutes after the addition of chloramine. Normally, however, the constant potential type of polarogram was employed, the potentials of -1.2 and -2.1 volts versus the pool being taken as standards to determine the heights of the chloramine and ammonium waves, respectively.

The Ilkovic equation states that the diffusion current, i_d, is proportional to $Ct^{1/6}$ where C is the concentration of the reducible species and t is the drop time of the electrode. Therefore to compare concentrations by means of diffusion current data, it is necessary to apply corrections to make allowance for changes in t with potential. This correction has been made in Figure 6, which shows the course of a typical decomposition. It will be seen that even though the residual current exhibits an ammonium wave and in spite of the fact that ammonium chloride was doubtless present as impurity in the chloramine (prepared by method D), no ammonium wave was observed until one hour after addition. After the appearance of the ammonium wave, its height exactly compensated for the decrease in the chloramine wave height and therefore the current at -2.1 volts versus the pool was independent of time. For experiments in which ammonium ion was in excess, $i_{2.1}$ was constant throughout the course of the decomposition and for all other experiments $i_{2.1}$ was constant after the passage of one-half life. Figure 7 shows another example of this behavior, although in this case
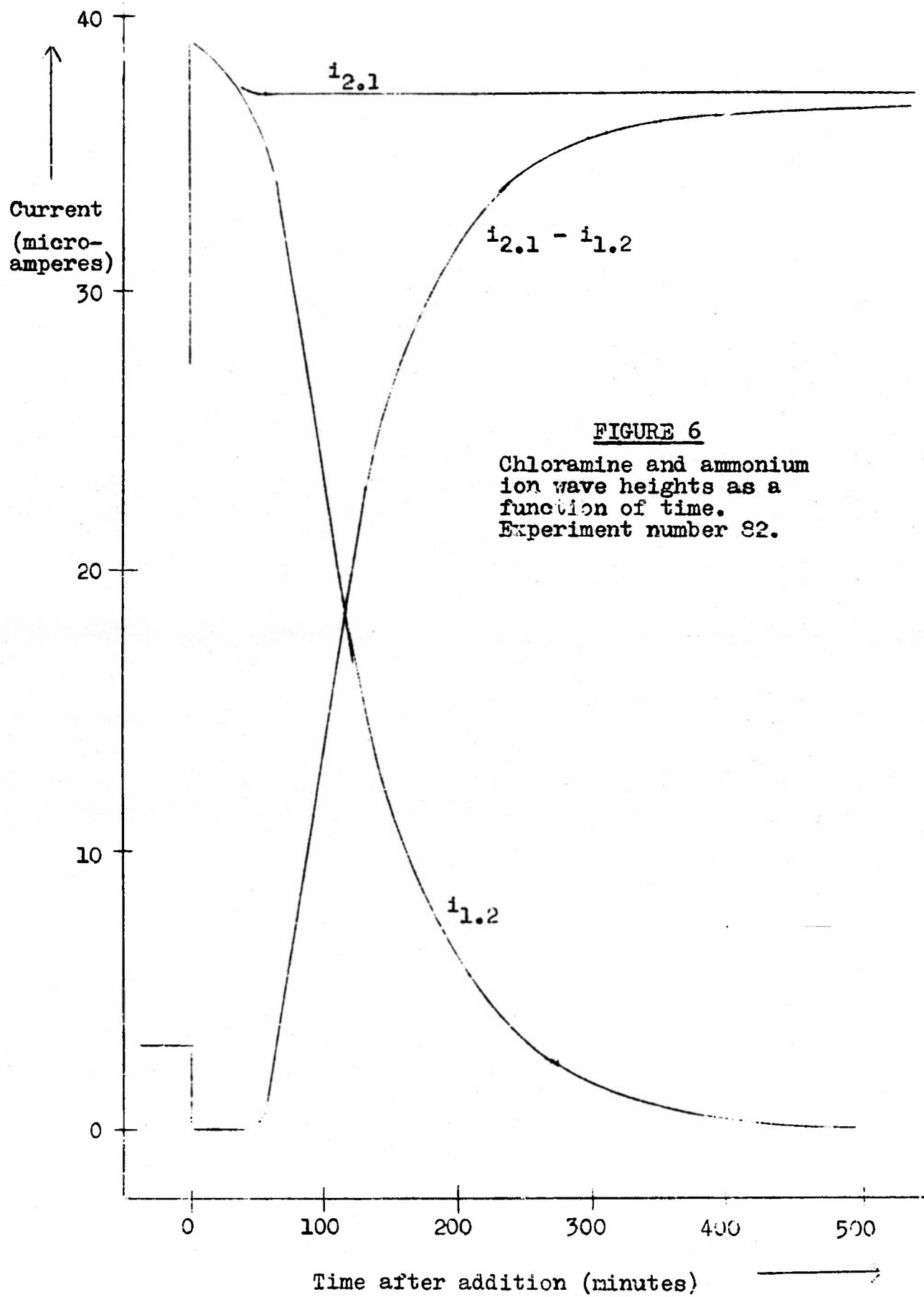
FIGURE 5

Successive polarograms of a solution of tetrabutyl-ammonium iodide at various times after the addition of chloramine; showing the increase in the ammonium ion wave height at the expense of that of chloramine.

29 minutes

45 minutes

60 minutes

107 minutes

157 minute

Current (micro-amperes)

Potential (volts versus pool)

FIGURE 6

Chloramine and ammonium
ion wave heights as a
function of time.
Experiment number 82.

FIGURE 7

Chloramine and ammonium
ion wave heights as a
function of time during
the initial stages of
chloramine decomposition.
Experiment number 71.
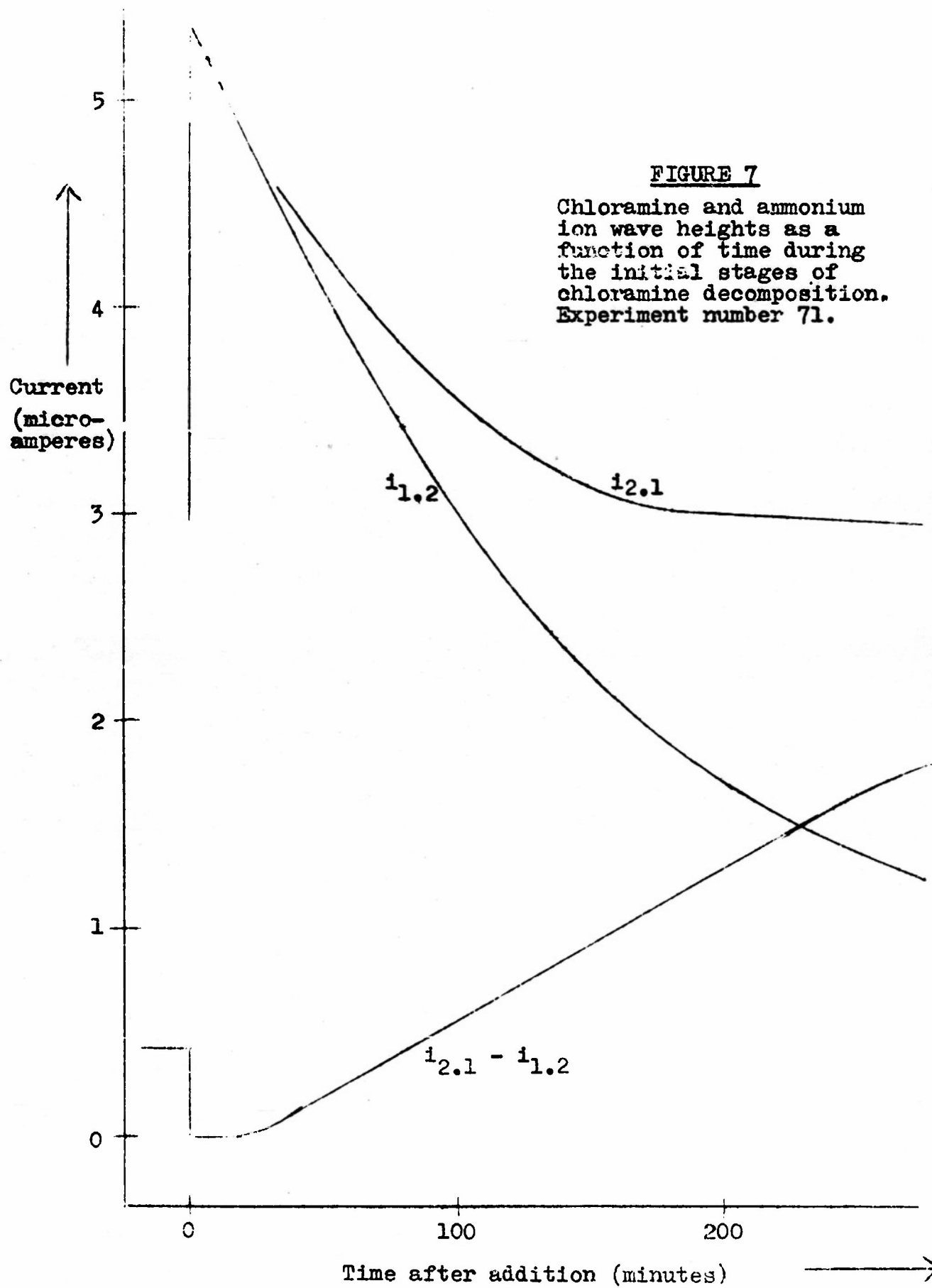
Table I

| Experiment Number	19	21	55	65	63	68	71	35	80	82
Supporting Electrolyte	Saturated Potassium Chloride Solution					0.5M NH$_4$Cl	Satd. tetrabutylammonium iodide solution			
Was the ammonia pre-dried over potassium metal?	Yes	No	Yes	Yes	No	Yes	No	Yes	Yes	Yes
Method of preparation of chloramine	C	C	D	D	D	C	D	C	D	D
Duration of region of curvature of log id versus time plot (minutes)	<10	<10	<25	45	25	15	<10	<20	30	70
Current (microamps) at -2.1 volts before introduction (less residual current)	Ammonium ion wave not determinable					"∞"	0.2	0.7	2.9	2.5
Current at -2.1 volt immediately after introduction, less current at -1.2 (corrected)						"∞"	0.0	19.0	0.0	0.0
Concentration of ammonium ion after introduction estimated from method	High	High	Low	Low	Low	Very high	Low	High	Low	Low
Initial chloramine wave height i.e. current at -1.2 V. extrapolated to instant of addition	1.26	3.63	17.4	22.5	30.2	32.3	5.32	10.0	11.2	38.0
Final half-life (minutes)	131	117	55	141	42	55	117	52	39	49

an ammonium wave was observed before the time at which $i_{2.1}$ commenced
to be constant.

Rotating Platinum Electrode - Experimental

A three-compartment cell was designed suitable for polarography
in liquid ammonia with a rotating microelectrode; it is shown
diagrammatically in Figure 8. The rotating electrode assembly,
operating through a mercury seal, is also shown in Figure 8. A cone-
drive motor was used to rotate the electrode. The shaft speed was
adjusted to 600 r.p.m. by oscillographic comparison with a 60-cycle
alternating potential.

Compartment C, the reference compartment, contained a platinum
sheet electrode of area 20 cm.^{2}. The microelectrode consisted of a
short length of platinum wire sealed through the end of a soda glass
capillary tube and inclined at an angle of about 20° to the vertical.
The approximate length of the exposed wire was 1.5 mm. and its
diameter was 0.35 mm.; the exposed area was thus about 1.8 mm.^{2}.
Electrical contact was made to the microelectrode by a copper wire
dipping into the open end of the capillary bore, which was filled with
mercury.

An electron electrode[3] was employed as reference. This con-
sisted of a solution of sodium in liquid ammonia in contact with the
platinum sheet. Such an electrode has been shown to function
reversibly, the electrode reaction being simply the passage of elec-
trons from the platinum into solution or vice versa:

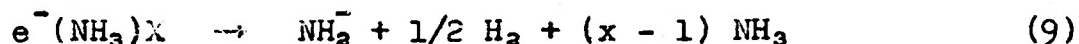$$e^-(Pt) \rightleftharpoons e^-(NH_3)_x$$
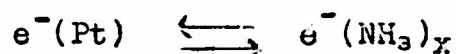
Solutions of sodium in liquid ammonia are unstable, giving rise to

FIGURE 8

Three-compartment cell and rotating platinum microelectrode assembly for polarography in liquid ammonia solutions.
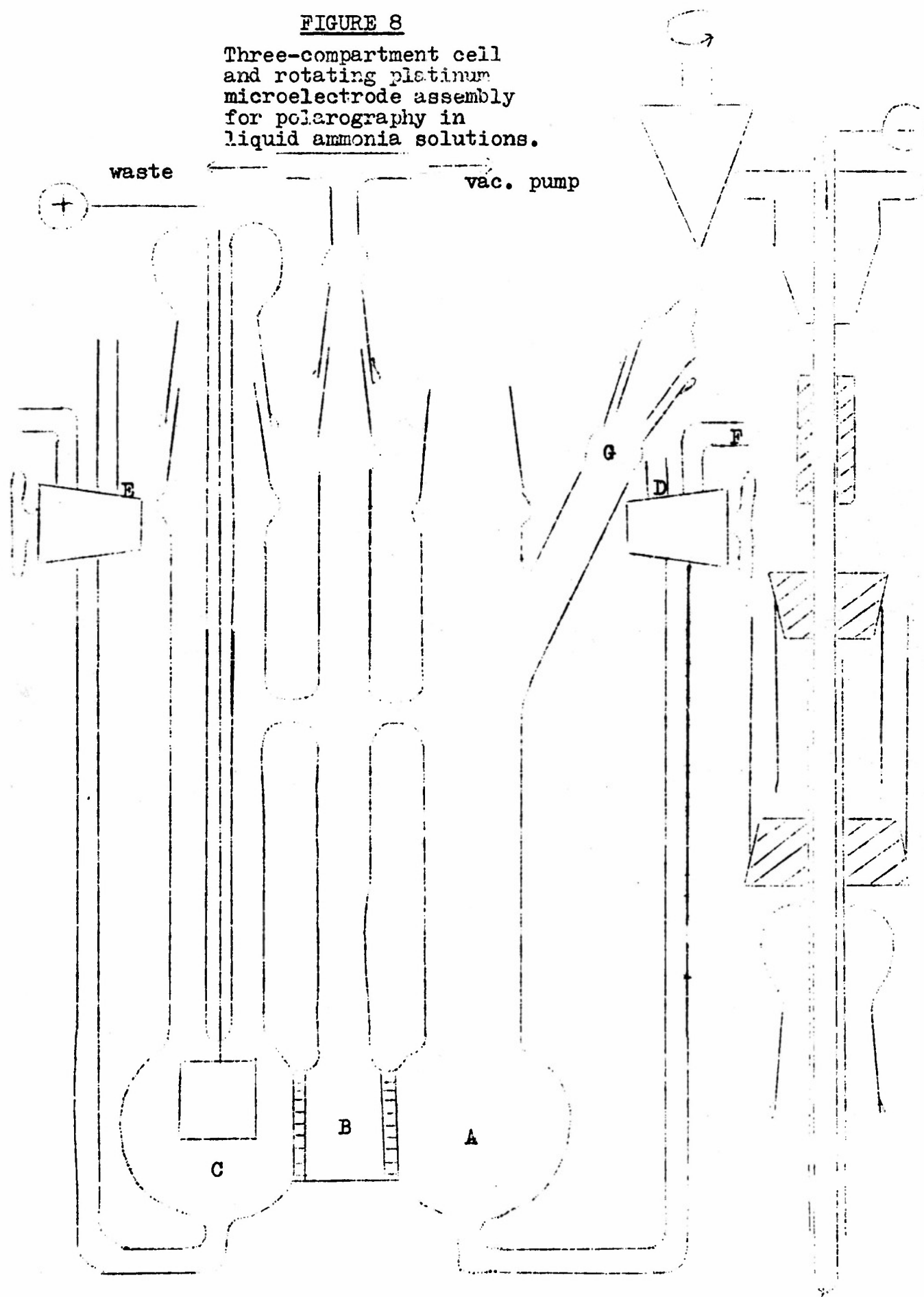
sodium amide by the reaction:

$$e^-(NH_3)x \rightarrow NH_2^- + 1/2\ H_2 + (x-1)\ NH_3 \qquad (9)$$

However such solutions can be kept at -78^oC. for from one to two weeks before this reaction is complete (as indicated by the fading of the characteristic blue color of the electron solution). When initially prepared the electron solution in compartment C was about 0.2 $\underline{M}$ in electrons, but thereafter the solution became more dilute on standing. A change of 0.030 volts in the potential of the electron electrode can be predicted[3] at -78^oC. for a 90% decomposition of the electron solution. Hence the electron electrode is not suitable as a reference of stable potential. However, during the course of a few days, the maximum time for which a given electron solution was retained, the electrode was sufficiently stable for the purposes of the present investigation. For short periods of time, the electron electrode is an excellent reference since it remains depolarized even at comparatively high current densities.

Compartment B, the "salt bridge", consisted of a saturated (about 0.15 $\underline{M}$ at -78^oC.) solution of sodium acetate standing over solid sodium acetate. The volume of compartment B was approximately 25 ml. Once hydrostatic equilibrium had been achieved, there was very little tendency for diffusion to occur through the frits separating B from compartments A and C. Occasionally a pale blue coloration could be observed in B, indicating some diffusion from C; the addition of a trace of ammonium acetate was sufficient to fade the color.

Compartment A had a volume of 100 ml. and contained a 0.1 $\underline{M}$ solution of sodium acetate in liquid ammonia, together with the

substance under investigation. The choice of a suitable supporting electrolyte for this system is based upon quite different criteria than for the dropping mercury electrode experiments. Alkali metal cations are not reduced at platinum cathodes in liquid ammonia and therefore sodium salts are permissible as supporting electrolytes. On the other hand, whereas halide ions can be used with mercury, large halide concentrations lead to anodic attack at platinum. The acetate ion was found to be quite suitable; it is not discharged either anodically or cathodically, nor is there any evidence of its being reduced by solutions of electrons. Recently, sodium perchlorate has been found to serve very satisfactorily as a supporting electrolyte. The total cell resistance was about 3000 ohms.

After the cell had been pumped at high vacuum for about an hour, it was flooded with nitrogen. A piece of clean sodium, about 8 mm. cube, was then placed into C and 0.82 gm. of sodium acetate were placed in each of the compartments A and B. The rotating electrode assembly was then placed in position, the whole cell was immersed up to the level of the cross-members in a solid carbon dioxide - ethyl cellosolve bath at -78°C. and ammonia was allowed to pass into the cell via stopcocks D and E. The flow rate was adjusted to maintain approximately equal levels in the three limbs and when the requisite volume of liquid ammonia had been condensed, a flow of nitrogen was substituted for the ammonia stream until equilibrium was achieved. The system was then ready for the recording of residual polarograms. Gaseous introductions were made via F; liquids and solids were added through the side arm G. After any addition, a stream of nitrogen was always passed through the cell to stir the contents and to expel any

dissolved oxygen.[3]

All polarograms were recorded with the Sargent Model XXI
Polarograph, with the cell at the sublimation temperature of carbon
dioxide, i.e. approximately -78°C., and at atmospheric pressure.

Rotating Platinum Electrode - Results

It was found that the rate and direction of polarization of the
rotating electrode had an effect upon the position of the recorded
curves along the potential axis, but that current readings were little
affected. Since current data were of interest in the present investi-
gation and because of the uncertainties in the reference electrode
potential, little attention has been given to the potential scale of
the polarograms. Most polarograms were recorded at a polarization
rate of 3.1 millivolts per second, the polarization of the rotating
electrode being increasingly cathodic.

In general, a residual polarogram showed a small cathodic wave
at about +0.9 volts versus the electron electrode. As in the experi-
ments with the dropping mercury electrode, this wave could be attri-
buted to the reduction of ammonium ions. Its height was increased
proportionally by the addition of small amounts of ammonium salts and
decreased proportionally with the number of coulombs passed when a
large current (of the order of 30 milliamperes) was passed cathodically
through the cell. This latter effect can be explained in terms of the
known reaction of electrons, liberated at cathodic potentials from the
rotating platinum electrode with ammonium ions:

$$e^-(NH_3)_x + NH_4^+ \rightarrow (x-1)NH_3 + 1/2\ H_2 \tag{9a}$$
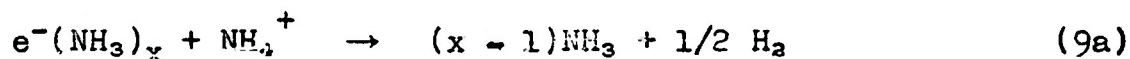
This effect served as a very convenient method of neutralizing the

liquid ammonia solution in compartment A. As long as an appreciable ammonium ion concentration existed in the cell, the blue color observed around the rotating electrode was restricted to the immediate vicinity of the electrode by virtue of reaction (9a). As neutrality was approached, the blue zone extended further into the solution and persisted for several seconds after the interruption of the current. With experience it became possible to "titrate" the solution accurately in this fashion to very low ammonium ion concentrations (as determined polarographically). It was important not to prolong the passage of current beyond the neutrality point, as this leads to the undesirable precipitation of sodium amide.

Polarograms of neutral solutions of liquid ammonia revealed an extensive region of potential in which there was virtually complete polarization (currents less than one microampere). This region extended from +3.0 volts versus the electron electrode (more positive than which, nitrogen evolution occurred) to 0.0 volts, the potential at which electron dissolution commenced. Transient maxima (both anodic and cathodic) were often observed on both residual and actual polarograms. The heights of these maxima were highly dependent upon the rate and direction of polarization of the rotating electrode and upon its previous history. Under constant potential conditions these spurious currents had only a transient existence. These effects are undoubtedly analogous to similar phenomena observed at platinum electrodes in aqueous solutions and which Kolthoff and Tanaka[17] have satisfactorily explained in terms of surface film formation.

Chloramine was observed to reduce at the rotating platinum electrode, giving an S-shaped cathodic wave of excellent symmetry and

with a well-defined diffusion current. The half-wave potential was somewhat irreproducible and values of +1.65±0.15 volts versus the electron electrode have been recorded.

Solutions of liquid ammonia containing both chloramine and ammonium salts gave a double wave, as exemplified in Figure 9. The first wave was identical with the reduction wave of chloramine, while the second had a half-wave potential of about +0.5 volts versus the electron electrode. That the second wave represented ammonium ion reduction was shown by the increase in its height following the addition of ammonium acetate. Apparently, the half-wave potential of the ammonium ion discharge had been shifted by some 400 millivolts by the prior reduction of chloramine.

The wave height of chloramine reduction at the rotating platinum electrode in liquid ammonia at -78°C. remained essentially constant over a period of 24 hours, showing that under these conditions chloramine is quite stable. The addition of hydrazine to such solutions resulted in a rapid decrease of chloramine wave height, the chloramine concentration being reduced to zero in about an hour.

Very few quantitative measurements were made with the system, because of lack of time. Some observations, however, were made that are significant in respect to the establishment of the mechanism of chloramine reduction; these results are quoted in Table 2.

FIGURE 9

Current-voltage plot of a liquid ammonia solution containing chloramine and ammonium salts; recorded using a rotating platinum microelectrode.
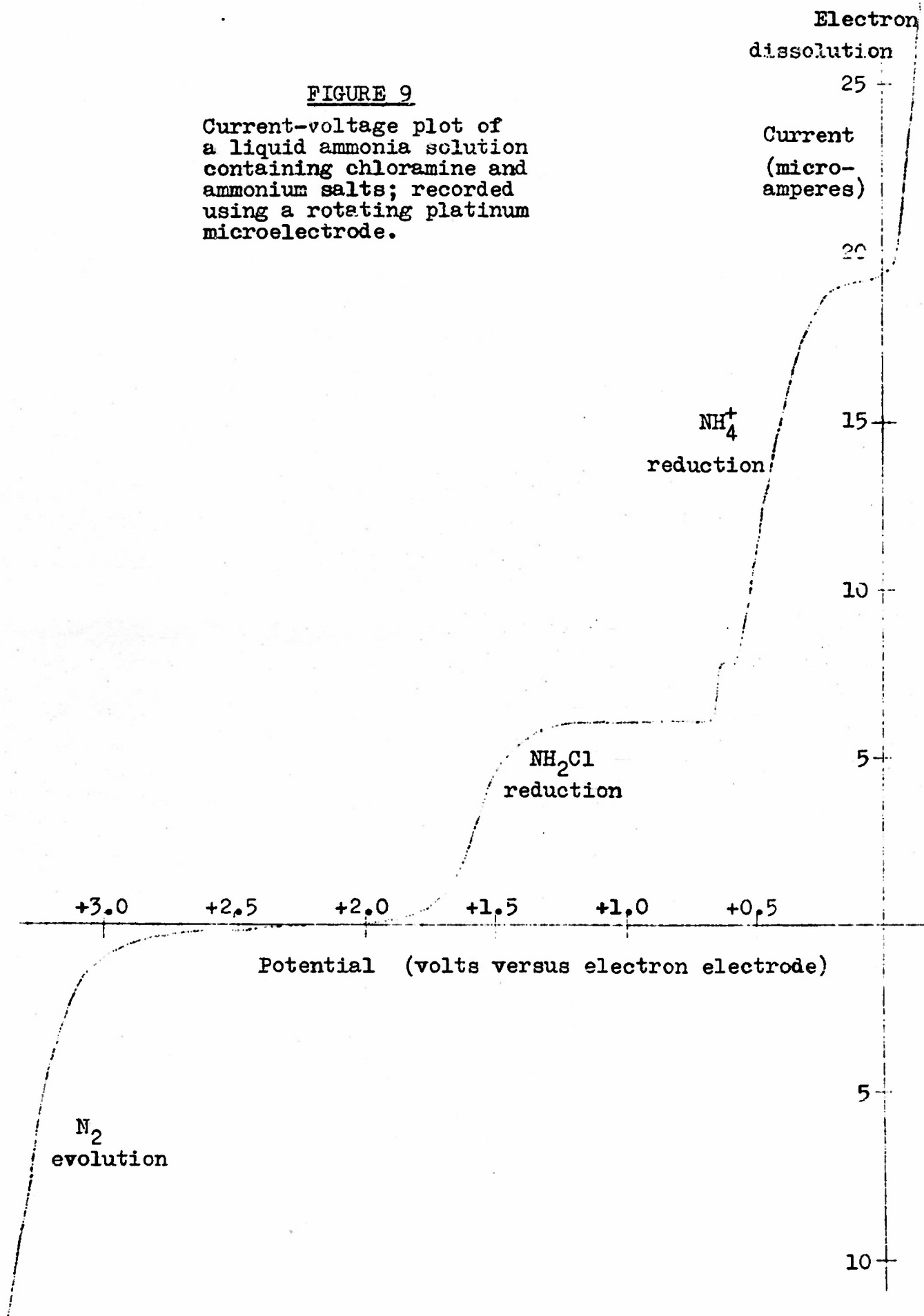
Table 2

|	Current at +1.0 volts (versus electrode (microamperes)	Current at +0.1 volts electrode)
Initially	0	< 1
After addition of ammonium acetate	0	11
After subsequent addition of neutral solution of chloramine in liquid ammonia (prepared by method H)	48	43
After subsequent addition of excess hydrazine and three hours standing	0	37

DISCUSSION OF MECHANISM OF CHLORAMINE DECOMPOSITION

A discussion of this subject is independent of the nature of the processes occurring at the dropping mercury electrode, or at the pool anode. The only supposition that is demanded is that of proportionality between the concentration of chloramine and the height of its reduction wave and this is extremely plausible in view of the diffusion control of the wave.

Other investigators have determined that the products of decomposition of chloramine in liquid ammonia solution are hydrazine, nitrogen and ammonium chloride.[13,18] Nitrogen and ammonium chloride are the major products, though hydrazine is formed in moderate yields. Hydrazine has been detected in the polarographic cell of the present investigation after all the chloramine had decomposed.

The decomposition may be formulated in terms of the two
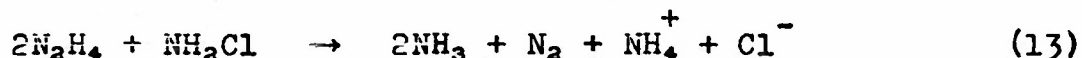
simultaneous reactions:

$$NH_2Cl + 2NH_3 \rightarrow N_2H_4 + NH_4^+ + Cl^- \tag{10}$$

and:

$$3NH_2Cl + 2NH_3 \rightarrow N_2 + 3NH_4^+ + 3Cl^- \tag{11}$$
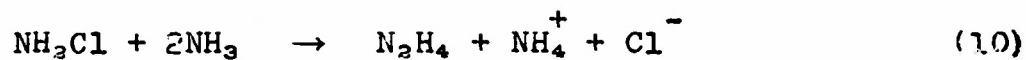
However, it is not necessary to invoke reaction (11), since the present investigation has confirmed earlier findings that hydrazine reacts rapidly with chloramine in liquid ammonia to give nitrogen. This last reaction may be written:

$$N_2H_4 + 2NH_2Cl \rightarrow N_2 + 2NH_4^+ + 2Cl^- \tag{12}$$

or, alternatively:

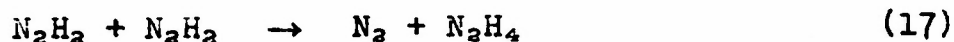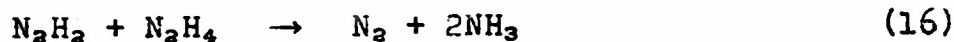$$2N_2H_4 + NH_2Cl \rightarrow 2NH_3 + N_2 + NH_4^+ + Cl^- \tag{13}$$

It is instructive to consider the situation from a kinetic standpoint. The initial reaction must be slow to account for the slow decay of chloramine:

$$NH_2Cl + 2NH_3 \xrightarrow{k_1} N_2H_4 + NH_4^+ + Cl^- \tag{10}$$
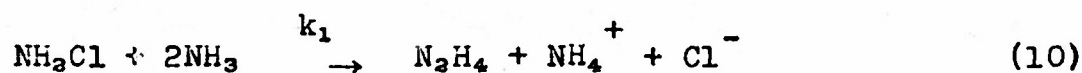
Reactions (12) and (13) involve three reactant molecules, but it is most unlikely that the rate-determining step involves a three body collision. A bimolecular reaction to yield an unstable species such as diimide seems much more plausible,

$$N_2H_4 + NH_2Cl \xrightarrow{k_2} N_2H_2 \ NH_4^+ + Cl^- \tag{14}$$
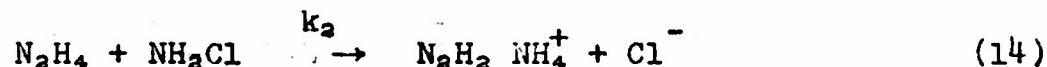
Several modes of decomposition may be envisaged for the transient diimide; of these, the following four would seem to be the most likely:

$$N_2H_2 + 2NH_3 \quad \rightarrow \quad 2N_2H_4 \qquad (15)$$

$$N_2H_2 + N_2H_4 \quad \rightarrow \quad N_2 + 2NH_3 \qquad (16)$$

$$N_2H_2 + N_2H_2 \quad \rightarrow \quad N_2 + N_2H_4 \qquad (17)$$

$$N_2H_2 + NH_2Cl \quad \rightarrow \quad N_2 + NH_4^+ + Cl^- \qquad (18)$$

It is possible that several of these reactions proceed concurrently or that other reactions may occur. However, it will be tacitly assumed that each reaction may occur independently and, furthermore, that each of the four reactions (15) to (18) proceeds at a faster rate than reaction (14).

If C and H represent, respectively, the concentrations of chloramine and hydrazine at any time, t, after the introduction of chloramine to the liquid ammonia, then kinetic reasoning based on the above assumptions leads to the equations:

$$\frac{dC}{dt} = -k_2C \left(\frac{k_1}{k_2} + yH \right) \qquad (19)$$

and

$$\frac{dH}{dt} = k_2C \left(\frac{k_1}{k_2} - xH \right) \qquad (20)$$

where x and y depend on the mechanism as listed in Table 3.

Table 3

Case	Mechanism	x	y
I	Reactions (10), (14) and (15)	-1	1
II	Reactions (10), (14) and (16)	2	1
III	Reactions (10), (14) and (17)	1/2	1
IV	Reactions (10), (14) and (18)	1	2

Equations (19) and (20) can be readily solved to obtain the following relationship between the concentrations of chloramine and hydrazine at any unspecified value of t

$$C_0 - C = \frac{(x + y)\ k_1}{x^2 k_2} \ln \left[\frac{k_1/k_2}{[k_1/k_2 - xH]} \right] - \frac{y}{H} H \tag{21}$$

where C_0 is the initial concentration of chloramine. However, to solve for C as a function of time requires the integration:

$$k_1 t = \int_0^F \frac{dF}{\left[\frac{k_2 C_0}{k_1} - \left(\frac{x + y}{x^2} \right) \ln \left(\frac{1}{1 - xF} \right) + \frac{yF}{x} \right] \left[1 - xF \right]} \tag{22}$$

where:

$$F = \frac{k_2 H}{k_1}$$

Equation (22) cannot be solved directly but it has been integrated arithmetically for various values of C_0 in cases III and IV. Cases I and II will not be considered further since they do not afford good agreement with experiment; case I, moreover, predicts a 100% yield of hydrazine, a condition not experimentally realized.

Figure 10 shows the results of these calculations, expressing the shape of the "first-order" decomposition plots as a function of initial chloramine concentration. It will be seen that for low initial concentrations the plot is linear throughout, with gradient independent of C_0. As the initial concentration of chloramine is increased, a region of curvature is developed early in the
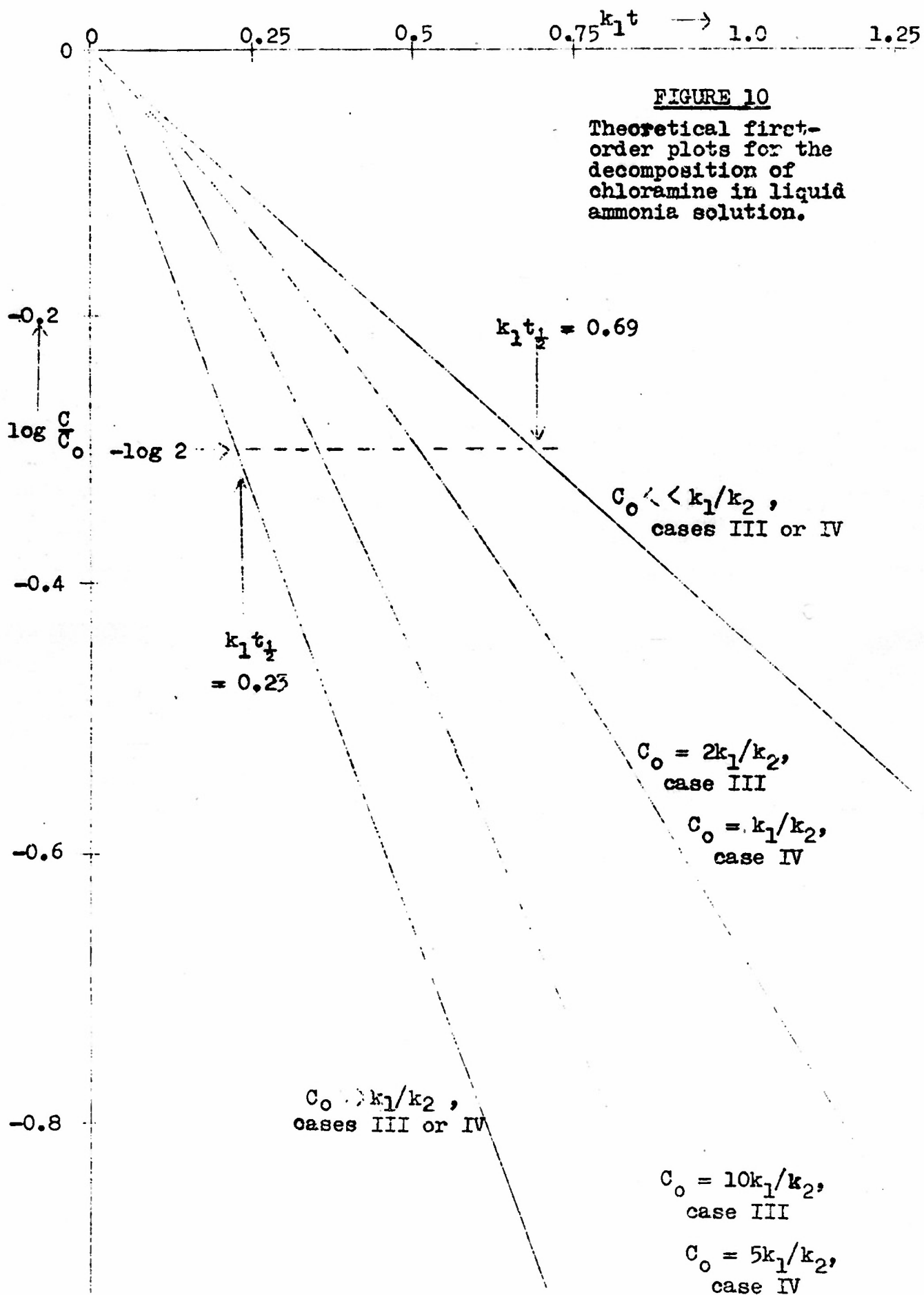
FIGURE 10

Theoretical first-order plots for the decomposition of chloramine in liquid ammonia solution.

decomposition. This region corresponds to the slow building-up of a steady state concentration of hydrazine. After the passage of about one half-life, effective linearity is achieved, the half-life increasing with C_0, to reach a limiting value exactly one-third of the half-life at low initial concentrations.

The experimental results will now be compared with the above theoretical findings, considering the aspects both of agreement and disagreement. In effect, this comparison is a comparison of Figures 3 and 10. In the following respects, the theory and experiment are in accord:

(1) At low initial concentrations of chloramine, the first-order plots are linear throughout.

(2) For low values of C_0, the slope of the log C versus time plot is independent of C_0, being characterized by a half-life of 127 ± 10 minutes.

(3) For initial concentrations of chloramine greater than that corresponding to a diffusion current of 0.5 microamperes, a higher rate of decomposition is, in general, observed.

(4) A region of curvature exists in the initial period of decomposition for all curves with the higher values of C_0.

(5) These higher curves approach a constant slope in one hour or less.

(6) When linearity of the higher curves is achieved, all curves, with one exception, have approximately equal slopes, of half-life 49 ± 6 minutes.

(7) The ratio of the half-life at low initial concentration to the final half-life at higher values of C_0 is 2.7 ± 0.5, in good

agreement with the theoretical value of 3.

Theory and experiment are at variance in regard to the following:

(1) Figure 10 would lead one to expect a more gradual transition between the two limiting values of the half-life than is observed. Experimentally, the half-lives fall into two definite groups with no intermediate values.

(2) Theory predicts a decrease in the duration of the region of curvature with increasing C_o. Experimentally this period is erratic but the trend is towards an increase in duration.

(3) One experimental curve (that for experiment 65) is in complete disaccord with the other curves and with the theory. Although it corresponds to a high value of C_o and exhibits curvature, its final half-life value corresponds to the family of curves with low C_o. This particular curve also displays another abnormality in that the current initially increased with time. No explanation can be given of this peculiar behavior.

The limited extent of the experimental data does not permit of an adequate evaluation of the adequacy of the postulated mechanisms. The mechanisms denoted by case III and case IV are equally capable of explaining some aspects of the experimental results, but fail equally with regard to other aspects. In the opinion of the author, the mechanism denoted by case IV is the more plausible, since case III requires a bimolecular disproportionation of a labile species. Without further data, it appears pointless to discuss possible explanations of the partial lack of agreement.

DISCUSSION OF MECHANISM OF CHLORAMINE REDUCTION

Since the limiting current of the reduction of chloramine at the dropping mercury electrode is diffusion controlled, its magnitude will be given by the Ilkovic equation:

$$i = k \, D_c^{1/2} \, n \, C \tag{23}$$

where C and D_c are respectively the concentration and diffusion coefficient of chloramine in the ammonia solution, n is the number of electrons involved in its reduction and k is approximately a constant for a given capillary under a given set of conditions.[5] The reduction of ammonium ions at the dropping mercury electrode[2] is known to be a one-electron process yielding ammonium amalgam:

$$NH_4^+ + e^- \xrightarrow{\text{Hg}} NH_4(\text{Hg}) \tag{24}$$
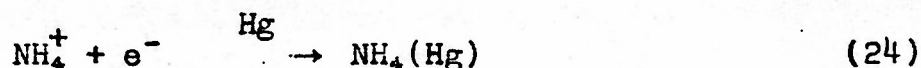
Application of the Ilkovic equation gives the following expression for the diffusion current of ammonium ion reduction:

$$i = k \, D_a^{1/2} \, A \tag{25}$$

where A and D_a are respectively the concentration and diffusion coefficient of ammonium ion in the liquid ammonia solution and k is almost identical with that in equation (23).

Unlike the diffusion coefficient of hydrogen ion in water, that of ammonium ion in liquid ammonia is not abnormally high. The apparent diffusion coefficient of ammonium ion in a saturated solution of tetrabutylammonium iodide in liquid ammonia at -36° C. may be calculated from the data of Laitinen and Shoemaker[2] to be

$4.1\pm0.3 \times 10^{-5}$ cm.^{2} sec.$^{-1}$. No data are available regarding the diffusion coefficient of chloramine in liquid ammonia, however, the diffusion coefficient of chloramine in aqueous solution has been determined polarographically[6] as 2.19×10^{-5} cm.^{2} sec.$^{-1}$. An estimate of the diffusion coefficient of chloramine in liquid ammonia at -36°C. may be made by assuming that this value bears the same ratio to the diffusion coefficients of thallous ion in the two systems, i.e.:

$$D_{NH_2Cl, NH_3, -36^\circ} \simeq \frac{D_{NH_2Cl, H_2O, 25^\circ} \times D_{Tl^+, NH_3, -36^\circ}}{D_{Tl^+, H_2O, 25^\circ}} \quad (26)$$

A more accurate estimate could be obtained by choosing an uncharged molecule as the calibrating species, however no data are available for such molecules in liquid ammonia. The use of an ionic species as a comparison introduces uncertainties due to the probable different degrees of solvation of the species in the two solvents; such an effect, however, should be minimized by the choice of an ion such as Tl^+ of large mass and low charge. Using the experimental data of Lingane and Kolthoff[7] and of Laitinen and Shoemaker[2] to evaluate the observed diffusion coefficients of thallous ion in the two solvents, application of equation (26) gives 3.6×10^{-5} cm.^{2} sec.$^{-1}$ as the approximate value of the diffusion coefficient of chloramine in liquid ammonia at -36°C. This value cannot be expected to be accurate; however it will be of the correct order of magnitude. For the purposes of the present discussion, it is sufficient to note that the diffusion coefficients of ammonium ion and chloramine are not very different in in liquid ammonia at -36°C. Hence the error caused by equating

$$D_c^{1/2} = D_a^{1/2} \qquad (27)$$

will be very small.

Accepting the approximations given above, the diffusion currents of chloramine and of ammonium ion are given by equations (23), (25) and (27) to be:

$$i_c = n K C \qquad (28)$$

and

$$i_a = K A \qquad (29)$$

where K is a constant.

All plausible mechanisms for the decomposition of chloramine (see e.g. equations (10), (11), (12), (14) and (18)) lead to the production of one mole of ammonium chloride per mole of chloramine decomposed. Hence if C_o and A_o represent, respectively, the initial chloramine and ammonium ion concentrations and C and A represent these concentrations at any subsequent time, then:

$$C_o + A_o = C + A = A_\omega \qquad (30)$$

where A_ω is the final ammonium ion concentration after complete decomposition of the chloramine.

Were it possible to obtain an accurate measure of C, equation (23) would enable n to be calculated directly by determining k, using the approximate value of D_c given above and so evaluating the nearest integral value of n in accord with equation (23). However, because of the labile nature of chloramine, this measurement cannot be made with certainty and so it is necessary to rely on an indirect method of determining n. It is most improbable that n will have values other

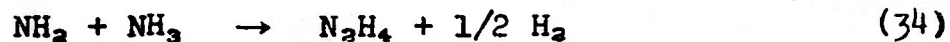than 1 or 2. If n = 2, the primary electrode reaction would be:

$$NH_2Cl + 2e^- \rightarrow NH_2^- + Cl^- \tag{31}$$
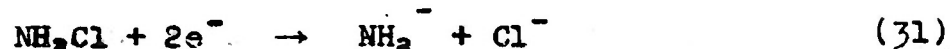
whereas if n = 1, the primary reaction would probably be:

$$NH_2Cl + e^- \rightarrow Cl^- + NH_2 \tag{32}$$

rapidly followed by

$$2NH_2 \rightarrow N_2H_4 \tag{33}$$

or by:

$$NH_2 + NH_3 \rightarrow N_2H_4 + 1/2 \ H_2 \tag{34}$$

Let consideration now be given to the current-voltage plot for the reduction, at a dropping mercury electrode, of a liquid ammonia solution containing, in addition to an excess of indifferent electrolyte, a concentration C of chloramine and a concentration A of ammonium ions. At a potential on the diffusion plateau of chloramine, but more positive than the reduction potential of ammonium ions, say at -1.2 volts versus the pool, the current will be simply given by (29):

$$i_{1.2} = i_c = n \ K \ C \tag{35}$$

At a potential on the diffusion plateau of the ammonium ion, say at -2.1 volts versus the pool, the form of the equation relating the current to the concentrations will depend on the value of n.

If n = 1, there is no interaction between the electrode processes (32) and (24) and hence the diffusion currents of ammonium

ion and chloramine will be strictly additive, thus:

$$i_{2.1} = i_c + i_a = K\,C + K\,A = K(C_o + A_o) = \text{a constant} \qquad (36)$$

On the other hand, if $n = 2$, there will be an interaction between the two electrode processes. The amide ion, a reduction product of reaction (31) is capable of reaction with ammonium ions diffusing to the electrode. Since the neutralization reaction:

$$NH_2^- + NH_4^- \quad \rightarrow \quad 2NH_3 \qquad (37)$$

may be presumed to be extremely rapid, there will be no reduction of ammonium ions until their bulk concentration exceeds that of chloramine. For an equimolar solution of chloramine and ammonion ion, the net electrode reaction would be:

$$NH_2Cl + NH_4^+ + 2e^- \quad \rightarrow \quad 2NH_3 + Cl^- \qquad (38)$$

Therefore for $n = 2$ we would expect:

$$i_{2.1} = i_{1.2} + K(A - C) = K(C_o + A_o) = \text{a constant} \qquad (39)$$

for $A > C$, while for $A \leqslant C$:
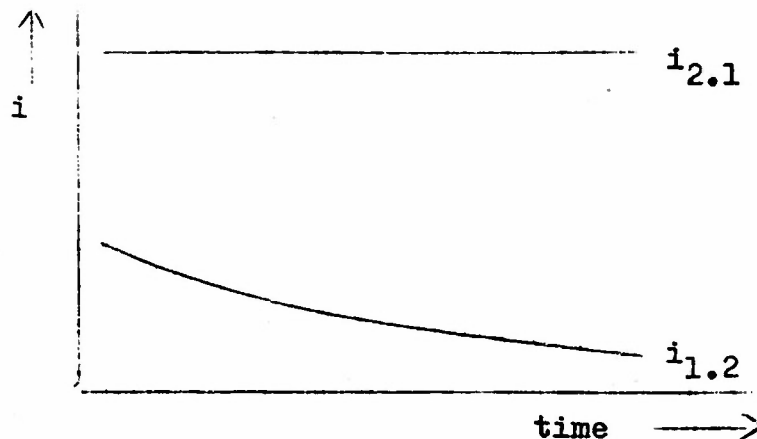
$$i_{2.1} = i_{1.2} = 2\,K\,C \qquad (40)$$

There are several analogous examples in aqueous polarography of interfering electrode reactions resulting in the non-additivity of diffusion currents.[8] For example, the reduction of oxygen in slightly acidic aqueous solutions results in the formation of hydroxyl ions which react with the diffusing hydrogen ions and prevent their reduction at modest concentrations.[9]
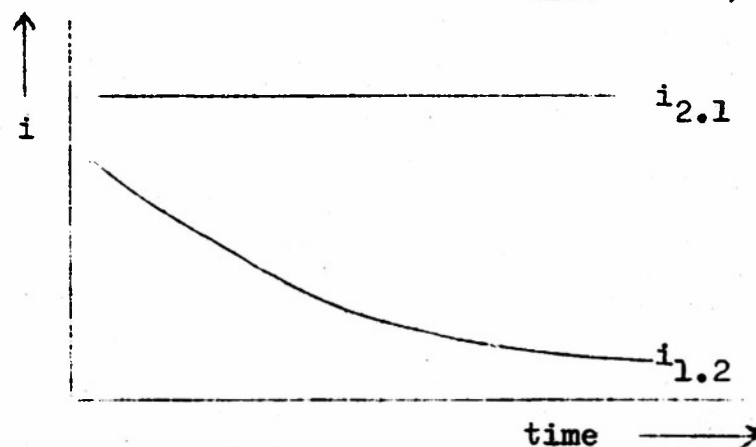
FIGURE 11

Theoretical diffusion current-time curves for a liquid ammonia solution containing chloramine and ammonium ion, the former decomposing to give the latter.
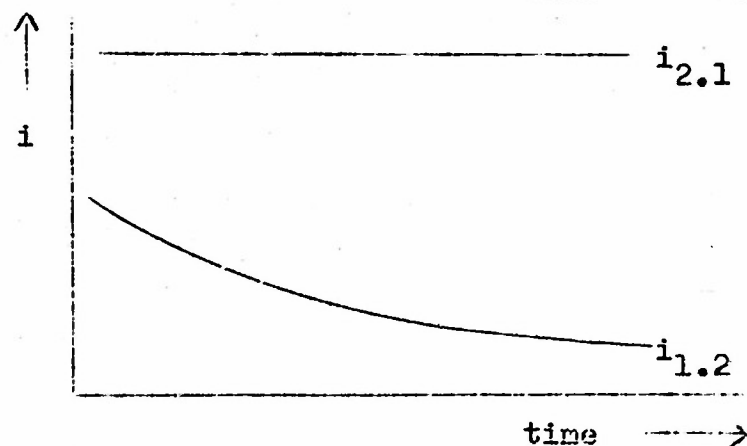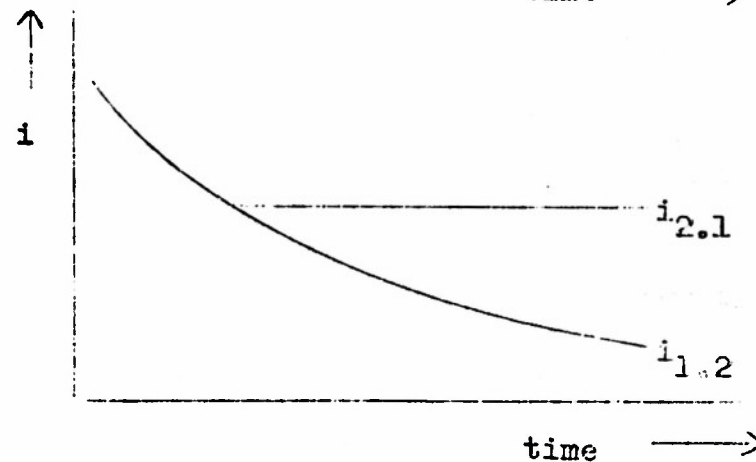
(a) $n = 1$, $A_o > C_o$

$i_{2.1}$

$i_{1.2}$

time $\longrightarrow$

(b) $n = 1$, $A_o < C_o$

$i_{2.1}$

$i_{1.2}$

time $\longrightarrow$

(c) $n = 2$, $A_o > C_o$

$i_{2.1}$

$i_{1.2}$

time $\longrightarrow$

(d) $n = 2$, $A_o < C_o$

$i_{2.1}$

$i_{1.2}$

time $\longrightarrow$

Consider now what the effect will be of observing the currents at -1.2 and -2.1 volts versus the pool, during the course of decomposition of a solution containing initially a concentration of C_0 of chloramine and A_0 of ammonium salts. The expected results can be predicted from the above equations and are shown diagrammatically for four cases in Figure 11. It is clear from the diagrams that since in the dropping electrode experiments no information was available concerning the values of C_0 and A_0, a decision as to the value of n can only be made by studying chloramine solutions of low acidity. Such was the case in experiments 82 and 71, the results of which are shown in Figures 6 and 7. These curves follow closely the type of behavior of Figure 11(d), indicating strongly that n = 2.

Another piece of evidence favoring a two-electron reduction of chloramine is to be found on examination of Table 1. It will be seen that in several experiments an ammonium wave existing in the residual polarogram disappeared on the introduction of the chloramine-containing gas stream. Such an effect cannot be explained on the basis of a one-electron reduction; on the contrary it would be expected that ammonium impurities in the gas stream would increase the height of the ammonium wave. An explanation in terms of the interfering electrode processes is, however, readily furnished by assuming that n = 2.

A third datum substantiating the two-electron reduction is to be obtained from the rotating platinum electrode experiment, the results of which are reported in Table 2. The function of the hydrazine in this experiment was simply to accelerate the decomposition of chloramine to an equimolar concentration of ammonium chloride. Again

there is qualitative support for n being equal to 2 in the observed
disappearance of the ammonium wave upon addition of chloramine. There
is also quantitative confirmation based on the current values.
Table 2 shows that $KA_0 = 11$ and that $KA_\infty = 37$. Equation (30) thus
gives $kC_0 = 26$. However $i_c = nKC_c = 48$ and the experimental value of
n is thus $48/26 = 1.85$, in close agreement with the theoretical
value 2.

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